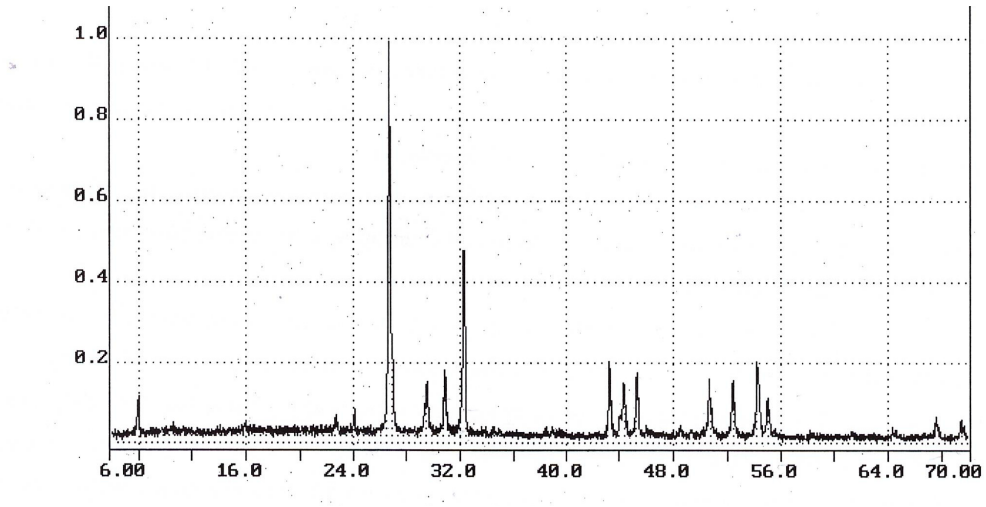
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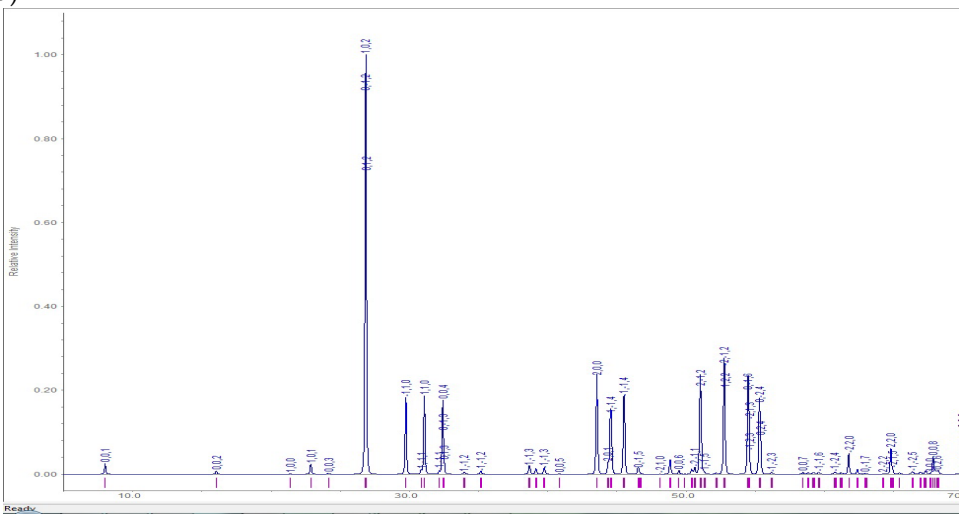
0.6
0.4
0.2
6.00
16.0
24.0
32.0
40.0
48.0
56.0
64.0
70.00

(a)


Relative Intensity
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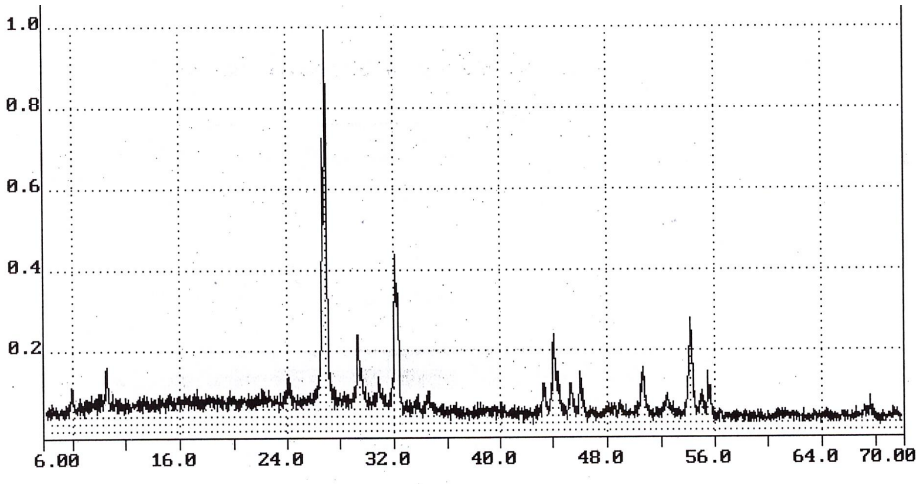
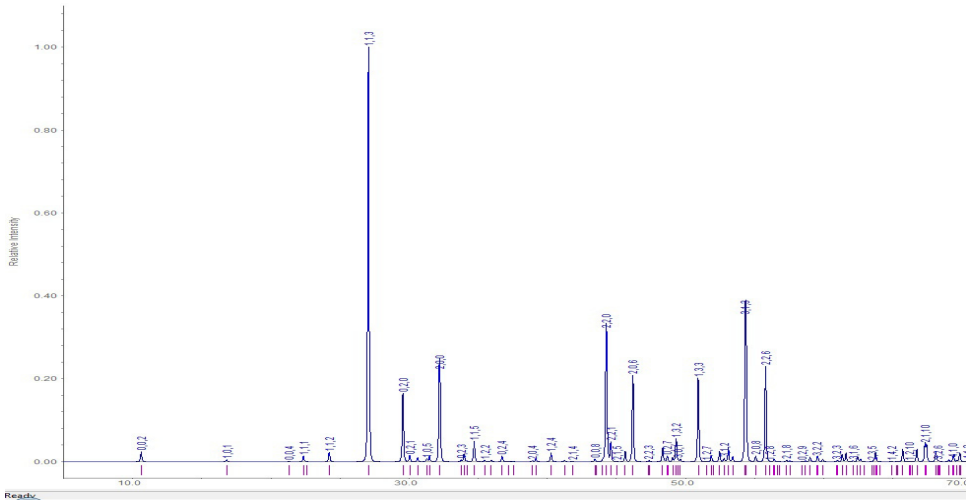
0.60
0.40
0.20
0.00
10.0
30.0
50.0
Ready

(b)


1.0
0.8
0.6
0.4
0.2
6.00
16.0
24.0
32.0
40.0
48.0
56.0
64.0
70.00

(c)



(d)

Figure S1 (a - d). Experimental powder diffraction pattern of $PbF(IO_3)$ crystals, DRON-UM diffractometer, Cu K_α radiation, 2θ-interval 6 – 70.0 °, **(a)** experiment, **(b)** simulated powder diffraction pattern for $PbF(IO_3)$ **(c)** total mass of crystals of experiment with predominance of $Pb(IO_3)_2$, **(d)** simulated powder diffraction pattern for $Pb(IO_3)_2$.

Table S1. Atomic coordinates and equivalent displacement parameters for $PbF(IO_3)$ orthorhombic unit cell. U_{equ} is defined as one third of the trace of the orthogonalized U*ij* tensor.

Atom	***x/a***	***y/b***	***z/c***	$\mathbf{U}_{equ}$, Å^2
Pb	0.66160(18)	0	0.13246(6)	0.0125(4)
I	0.1319(8)	0	0.36824(11)	0.0132(12)
F	0.883(2)	0.25	0	0.014(3)
O1	0.361(3)	-0.150(3)	0.3022(18)	0.0149(13)
O2	0.282(3)	-0.249(3)	0.4296(16)	0.012(4)
O3	0.034(4)	-0.124(3)	0.222(2)	0.018(4)

Table S2. Interatomic distances for $PbF(IO_3)$ orthorhombic unit cell.

Bond	**Distance,** Å	**Bond**	**Distance,** Å
Pb – F (x2)	2.458(7)	Pb – O3 (x2)	2.51(2)
Pb – F (x2)	2.659	Pb – O3 (x2)	2.57(2)
Average	2.558	Average	2.54
I – O1 (x2)	1.79(2)		
I – O2 (x2)	1.832(19)		
I – O3 (x2)	1.86(2)		
Average I – O	1.827		

Table S3. Atomic coordinates and equivalent displacement parameters for $PbF(IO_3)$ monoclinic unit cell. U_{equ} is defined as one third of the trace of the orthogonalized U*ij* tensor.

Atom	***x/a***	***y/b***	***z/c***	$\mathbf{U}_{equ}$, Å^2
Pb	0.6616(2)	-0.6616(2)	0.13207(3)	0.00514(18)
I	0.1299(5)	-0.1290(5)	0.36880(7)	0.0061(4)
F1	0.147(3)	-0.634(4)	-0.003(2)	0.0105(18)
O2	0.154(4)	0.081(3)	0.2217(13)	0.015(2)
O4	0.533(3)	-0.034(3)	0.4317(14)	0.015(2)

O7	0.195(4)	-0.516(4)	0.3042(16)	0.019(3)

Table S4. Interatomic distances for $PbF(IO_3)$ monoclinic unit cell

Bond	**Distance, Å**	**Bond**	**Distance, Å**
Pb – F1	2.421(16)	Pb – O2	2.527(15)
Pb – F1	2.510(17)	Pb – O2	2.553(15)
Pb – F1	2.62(2)		
Pb – F1	2.616(17)		
Average	2.542	Average	2.54
I – O7	1.790(17)		
I – O4	1.840(15)		
I – O2	1.845(14)		
Average I – O	1.825		